

# Fingerprints of antiaromaticity in the negative ion (Li<sub>3</sub>Al<sub>4</sub>)<sup>−</sup> via an *ab initio* quantum-chemical study

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## Abstract

Fingerprints of antiaromaticity in the negative ion (Li<sub>3</sub>Al<sub>4</sub>)<sup>−</sup>, this species being realizable via a laser vaporization technique, are revealed by means of an *ab initio* quantum-chemical investigation. First, the ground-state equilibrium geometry of this ion is predicted. Also, the characteristics of the HOMO are studied, both for the square and the rectangular Al<sub>4</sub> geometry in two low-lying isomers of the negative ion. There is no particular sensitivity to the change in geometry of the Al<sub>4</sub> configuration. Therefore, we have calculated theoretically chemical shifts, which contain remarkable fingerprints of antiaromaticity. As to future directions, some comments are added in relation to the Shannon entropy.

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## 1. Background and outline

The present study uses *ab initio* quantum-chemical calculations to treat the metal aromaticity of  $(\text{Li}_3\text{Al}_4)^-$  very specifically. However, for background, it is important to record first of all the extensive review by Boldyrev and Wang [1] on all-metal aromaticity and antiaromaticity. Of particular relevance for the present article is Section 7 of their review, which refers to  $(\text{Li}_3\text{Al}_4)^-$ . It is also relevant here to stress that Schleyer *et al.* [2] tested aromaticity in the  $\text{Al}_4^{2-}$  dianion using nucleus-independent chemical shifts (NICS) proposed by Schleyer *et al.* earlier [3].

With this as background, the outline of our present work is as follows. In Section 2 immediately below, we record quantum-chemical predictions of the geometries of two low-lying isomers of  $(\text{Li}_3\text{Al}_4)^-$ . We also carry out there a stability test of these two geometries, which is positive, the normal mode vibrational frequencies being tabulated, as well as other HOMO properties of these isomers. Section 3, which with the geometries in Fig. 1 is at the heart of the present study, deals quantitatively with chemical shifts, which are shown to contain very pronounced fingerprints of antiaromaticity in  $(\text{Li}_3\text{Al}_4)^-$ .

## 2. Quantum-chemical prediction of geometries of low-lying isomers of $(\text{Li}_3\text{Al}_4)^-$

The quantum-chemical *ab-initio* calculations have been performed using the Gaussian 09W package [4]. All the structures were energy optimized with second order Møller-Plesset (MP2) [5, 6, 7, 8, 9, 10] perturbation method, considering all the valence and core electrons (MP2=FULL) at the 6-311G [11, 12] level of the theory, adding polarization (d,p) [13] and diffuse (++) [14] functions. Local minima were attained with the program's default geometry optimization (Berny algorithm) [15] procedure and settings. To obtain a square planar structure for the four Al atoms, we constrained the four Al-Al distances to be equal with the valence angles at  $90.0^\circ$ . Nuclear magnetic resonance (NMR) Shielding Tensors were obtained with the Gauge-Independent Atomic Orbital (GIAO) method [16] for the optimized MP2 structures.

Fig. 1 shows the geometry thereby predicted for two low-lying isomers of the negative ion under discussion. Fig. 1a we have anticipated to have the anti-aromatic species, with the Al nuclei on the vertices of a slightly distorted rectangle. In contrast, Fig. 1b shows the  $\text{Al}_4$  square geometry, the common bond-length being  $\sim 2.637 \text{ \AA}$ .

Anti-aromatic (Fig. 1a)	Aromatic (Fig. 1b)
125.0279	123.0215
140.9736	152.2599
153.7713	167.7396
157.0725	178.0138
188.7271	208.0585
220.1328	217.0149
233.7731	224.6717
234.4931	260.3682
239.0553	265.0598
299.0800	266.4721
323.5899	296.6529
330.2183	336.9039
341.5039	353.8490
361.6591	357.7507
375.4484	373.3925

Table 1: Normal mode vibrational frequencies (in a.u.) for both isomers shown in Fig. 1.

As a stability test, we record in Table 1 the normal mode vibrational frequencies for both isomers shown in Fig. 1. The overall range of frequencies is practically the same in the two cases, though differences of detail are in evidence. Both isomers predicted in Figs. 1a and 1b pass the stability test, all the frequencies in Table 1 being real.

In Fig. 2 (left column), we have thought it of interest to record the shapes of the HOMO orbitals of the anti-aromatic isomer, together with the corresponding eigenvalues. Fig. 2 (right column) shows similar results for the other low-lying isomer, and it is fair to say that no very clear fingerprints are in evidence in comparing the two geometries of the negative ion in Fig. 2

Therefore, we turn immediately to discuss where we have found quite distinct fingerprints of antiaromaticity, namely in chemical shifts.

### 3. Theoretically predicted chemical shifts

This Section finds its motivation in the review of Schleyer *et al.* [2]. These authors consider there nucleus-independent chemical shifts (NICS) as an aro-

$E$ (MP2) (Hartree)	Anti-aromatic −990.91594	Aromatic −990.91340
	ppm	ppm
Li-1	44.0	−59.4
Li-2	37.0	−82.5
Li-3	102.0	102.4
Al-1	531.2	572.0
Al-2	531.2	575.9
Al-3	719.8	734.3
Al-4	719.8	735.8

Table 2: Total MP2 energies (Hartree) of ground-state isomers of  $(\text{Li}_3\text{Al}_4)^{-1}$ , along with their MP2 GIAO Magnetic Shielding in ppm. See Fig. 1 for numbering scheme.

maticity criterion. The development of the original NICS technique emerged from the study of ring current effects on  $\text{Li}^+$  chemical shifts described in the above review.

To match the customary NMR convention, NICS indices correspond to the negative of the magnetic shielding computed at chosen points in the vicinity of molecules. NICS is normally computed at ring centres, at points above, and even at grids in and around the molecule. Significantly negative NICS values in interior positions of rings or cages indicate the presence of induced diatropic ring currents (aromaticity), whereas positive indices at each point imply paratropic ring currents and antiaromaticity. With this brief background, our results follow.

Table 2 records first the second order Møller-Plesset (MP2) energies in Hartrees for the two low-lying isomers of Fig. 1. The antiaromatic case lies lower, though the energy difference is but 0.0025 Hartrees. But the Li shifts are seen from Table 2 to be dramatically different from the (almost) rectangular  $\text{Al}_4$  configuration and the square geometry. In fact, for the two Li atoms above and below the  $\text{Al}_4$  plane, namely Li-1 and Li-2, there is a much bigger downfield shift for the square configuration (−59.4 and −82.5) than for the rectangular one (44.0 and 37.0). While for the external one, Li-3, in both cases the shift is around 102, which is consistent with the value calculated at the same level of the theory for isolated Li system ( $\text{Li} = 101.4$ ;

$\text{Li}^{+1}=93.3$ ;  $\text{Li}^{-1}=104.4$ ).

For the Al atoms the situation is reversed, there is a bigger downfield shift for the rectangular configuration with a much smaller relative change, compared to the Li atoms, with respect to the values for the isolated Al system ( $\text{Al} = 787$  [17];  $\text{Al}^{+1} = 784$ ;  $\text{Al}^{+2} = 776$ ;  $\text{Al}^{+3} = 766$ ).

#### 4. Summary and future directions

The important predictions of the present *ab initio* quantum chemical study are: (i) The geometries of the two low-lying isomers shown in Fig. 1. Here, in Fig. 1a the anti-aromatic almost rectangular form of the  $\text{Al}_4$  nuclei is shown, while the square  $\text{Al}_4$  configuration is as predicted in Fig. 1b; (ii) The vibrational frequencies of these two isomers, which are recorded in Table 1; (iii) Most important, the chemical shifts we predict from the present theoretical investigation are the really sensitive fingerprints of antiaromaticity, as is clear from Table 2.

As to future directions, we want to mention the interest in the Shannon entropy. This has gained renewed attention by the appearance of the work by Noorizadeh and Shakerzadeh [18]. These authors have proposed a novel measure of aromaticity based on the local Shannon entropy in information theory. Their index, which measures the probability of electronic charge distribution between atoms in a given ring, is termed by them the Shannon aromaticity (SA). These authors observed linear correlations between the SAs they evaluated by density functional theory (DFT) [19], and other criteria of aromaticity, such as ASE, A and NICS indices, the last of these being emphasized in our present study on the ion  $(\text{Li}_3\text{Al}_4)^-$ .

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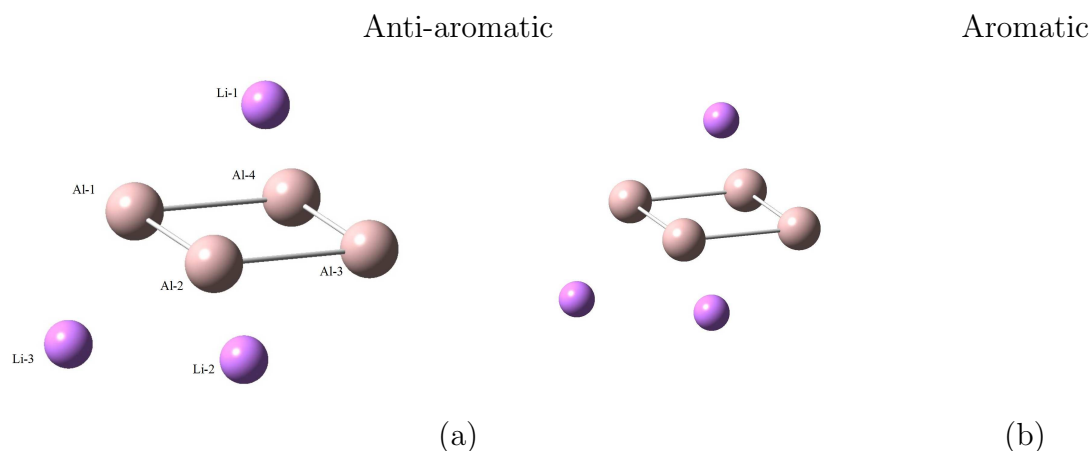


Figure 1: Structure of  $(\text{Li}_3\text{Al}_4)^{-1}$  and numbering scheme.

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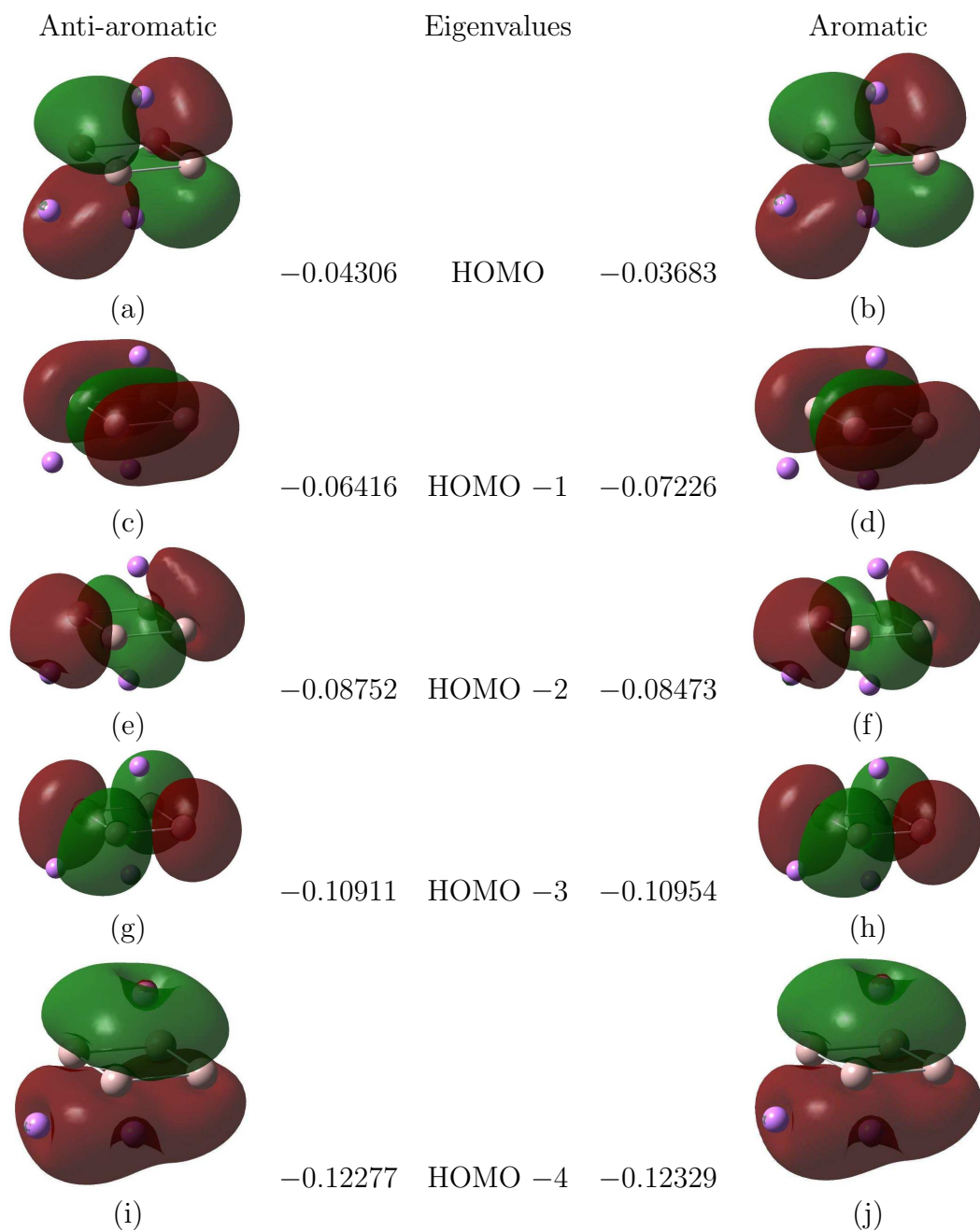


Figure 2: (Color online) HOMO orbitals of the anti-aromatic (left) and aromatic (right) isomers, and corresponding eigenvalues.